



SPECTROSCOPY

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Block – 3 : Spectroscopy – I

Lecture-1

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❖ LEARNING OUTCOMES

After studying this Chapter, you shall be able to:

- What is spectroscopy
- Types of Spectroscopy
- Understand what is electromagnetic radiation.
- Analyze the electromagnetic spectrum .
- Understand concept of UV-Visible spectroscopy.
- Learn about the possible electronic transitions.
- To Know about absorption shift and band
- To know about Absorption law

INTRODUCTION:

The Interaction of Electromagnetic Radiation (EMR) with sample is known as Spectroscopy. It is a part of analytical Chemistry which is used for the identification of any unknown substances.

Types of Spectroscopy: Initially Spectroscopy can be categorized into the following two types.

1. Absorption spectroscopy

2. Emission Spectroscopy

1. Absorption spectroscopy:

When a sample absorbs a certain amount of EMR, some of the EMR is absorbed by the compound present in the sample and will give rise to a spectrum which is called as absorption spectrum and

that branch of spectroscopy are known as absorption Spectroscopy.

2. Emission Spectroscopy:

When the EMR is introduced in a sample than the molecule is excited by the absorption of some EMR , after excited molecule come back in its original state by the emission of energy in the form of radiation which are emitted by the excited molecule will give rise a spectrum which is called as Emission spectrum and that branch of Spectroscopy is known as Emission Spectroscopy.

Some other Spectroscopy types are given as:

- 1. Electronic Spectroscopy*
- 2. Infrared Spectroscopy*
- 3. Microwave Spectroscopy*

3. Raman Spectroscopy

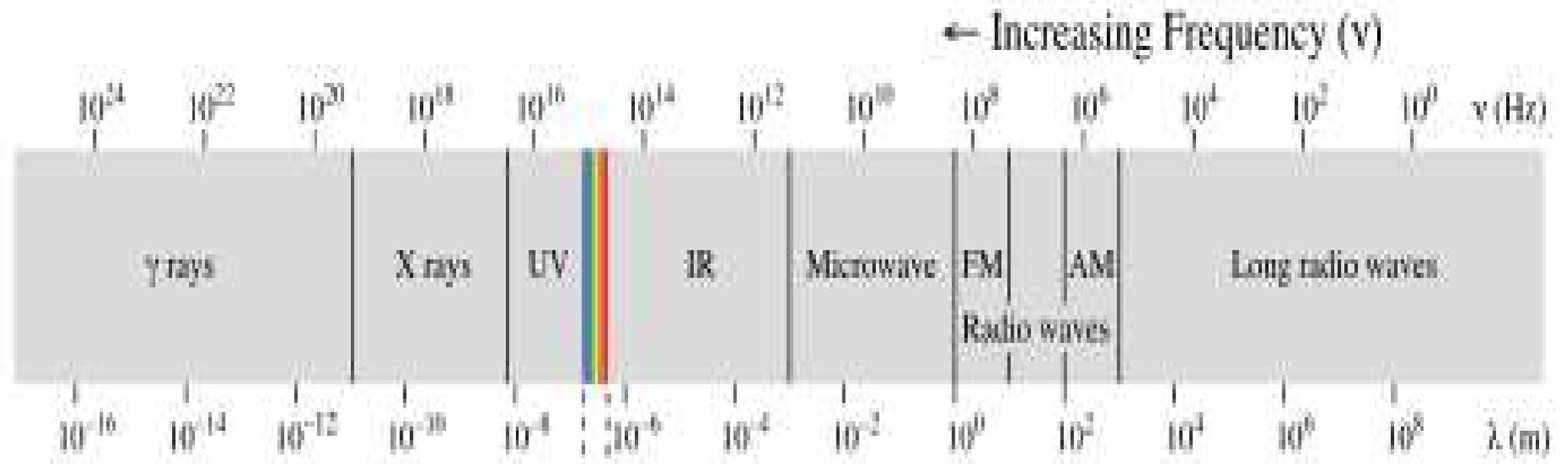
4. Nuclear Magnetic Resonance Spectroscopy (NMR)

5. Mass Spectrometry

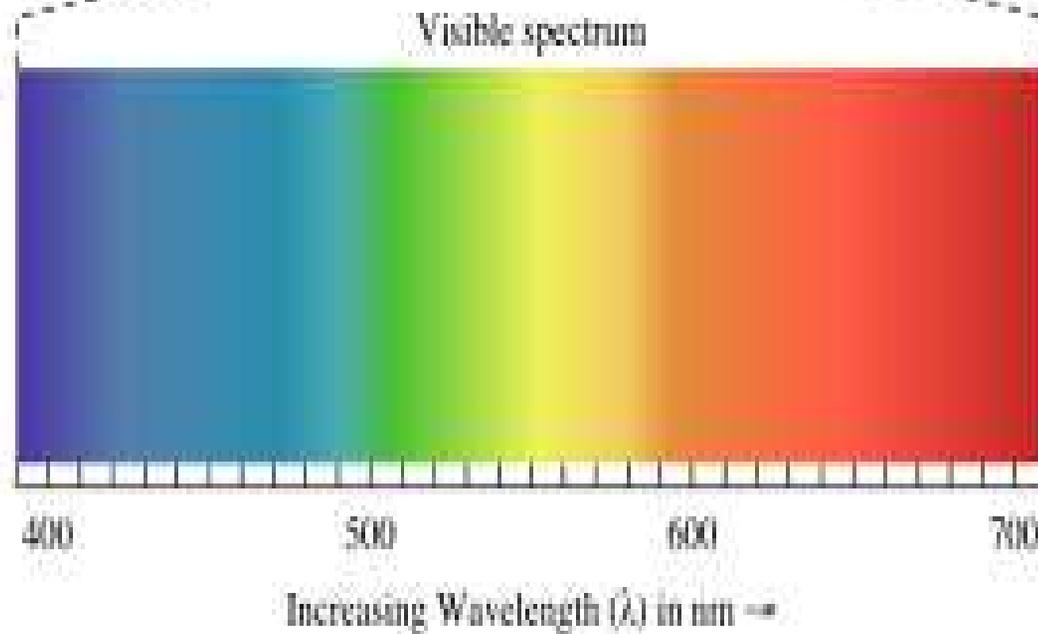
Here we will discuss about the various aspects of different spectroscopic techniques and more specifically about UV-spectroscopy and its uses.

➤ *ELECTROMAGNETIC RADIATION AND SPECTROSCOPY:*

The arrangement of all types of radiations in the order of their increasing wavelength or decreasing frequencies is known as electromagnetic (EM) spectrum. The electromagnetic spectrum includes radio and TV waves, microwaves, infrared, visible light, ultraviolet, X-rays, γ -rays, and cosmic rays, as shown in the **Figure 1**.

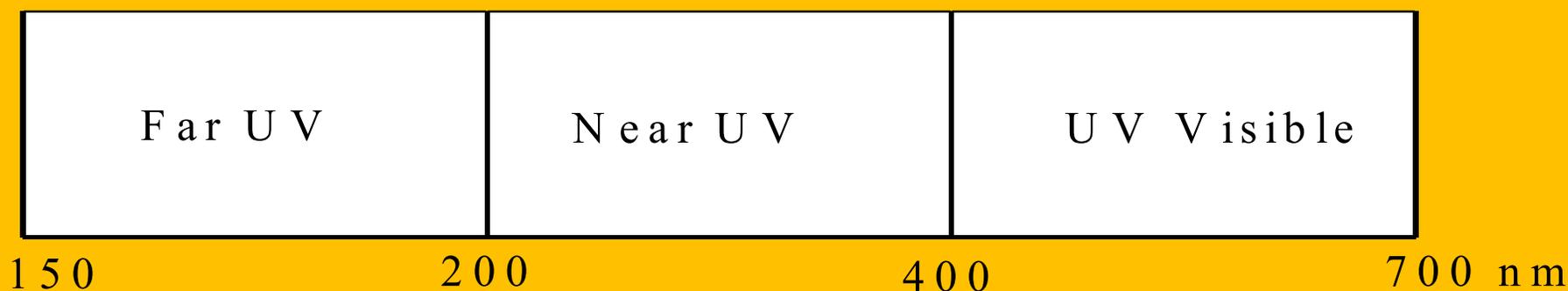


Increasing Wavelength (λ) →



❖ ULTRAVIOLET–VISIBLE SPECTROSCOPY (ELECTRONIC SPECTROSCOPY):

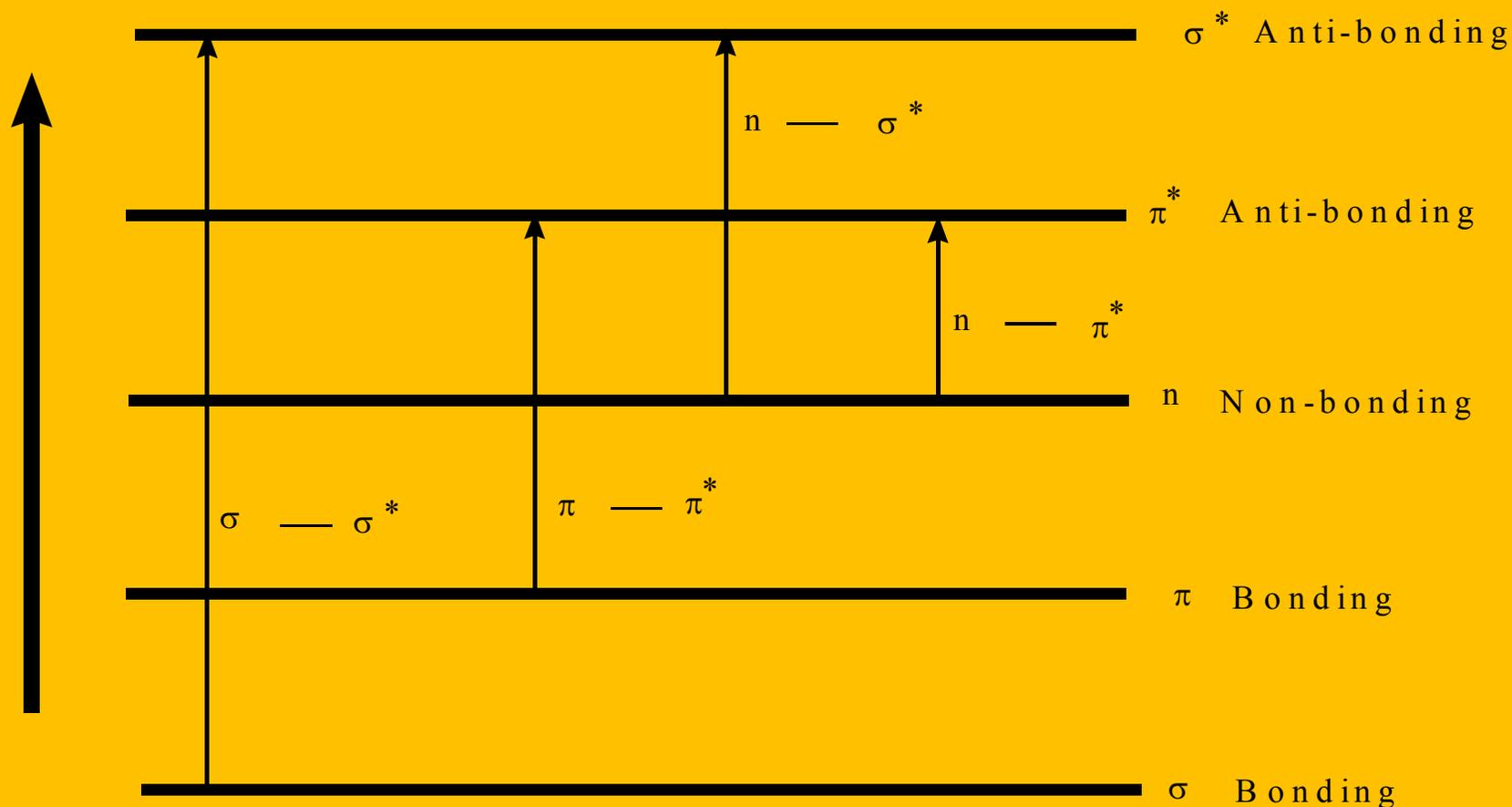
UV-Visible spectroscopy deals with the study of the electronic transitions of molecules as they absorb light in the UV (190-400 nm) and visible regions (400-800 nm) of the electromagnetic spectrum. The absorption of ultraviolet or visible radiation lead to transition among electronic energy levels, hence it is also often called electronic spectroscopy. The UV radiation are ranging from 1500 Å⁰ 4000 Å⁰ or 150-400nm. UV region is also divided in to three different parts which are given below:



❖ *TYPES OF ELECTRONIC TRANSITIONS*

The ground state of an organic molecule contains valence electrons in three principal types of molecular orbitals, namely σ orbitals, π orbitals and filled but nonbonding orbitals (n). Both σ and π orbitals are formed from the overlap of two atomic or hybrid orbitals. Each of these molecular orbitals therefore has an antibonding σ^* or π^* orbital associated with it. An orbital containing n electrons *does not have an antibonding orbital because it is not formed from two orbitals*. Sigma bonding orbitals have lower energy than π bonding orbitals, which in turn have lower energy than non-bonding orbitals. In the Electronic transitions, promotion of an electron from one of the three ground states (σ , π , or n) to one of the two excited states (σ^* , or π^*) takes place.

As a result, there are six possible transitions- σ to σ^* , σ to π^* , π to π^* , π to σ^* , n to π^* , n to σ^* . The most commonly observed transitions and their relative energies are summarized in **Figure 2**.



Electronic Transitions in UV spectroscopy

1) σ to σ^* Transition:

A transition of electrons from a bonding sigma orbital to the antibonding sigma orbital is designated as σ to σ^* transition. These are high energy transitions as σ bonds are generally very strong. Thus these transitions involve very short wavelength ultraviolet light (< 150 nm) and usually fall outside the range of UV-visible spectrophotometers (200-800 nm).

Alkanes can only undergo σ to σ^* transitions.

2) π to π^* Transition:

The transition of an electron from a π bonding orbital to a π^* antibonding orbital is designated as π to π^* transition. These types of transitions take place in compounds containing one or more unsaturated groups like simple alkenes, carbonyl, aromatics, nitriles, nitro etc.

3) n to σ^* Transition:

The transition of an electron from a non-bonding orbital to the antibonding sigma orbital is designated as n to σ^* transition. Saturated compounds containing atoms with lone pairs (nonbonding electrons) like saturated alcohols, amines, halides, ethers etc are capable of showing n to σ^* transitions. Energy required for these transitions is usually less than σ to σ^* transitions.

4) n to π^* Transition:

The transition of an electron from a non-bonding orbital to a π^* antibonding orbital is designated as n to π^* transition. This transition involves the least amount of energy in comparison to all other transitions and therefore gives rise to an absorption band at longer wavelength.

❖ SELECTION RULE:

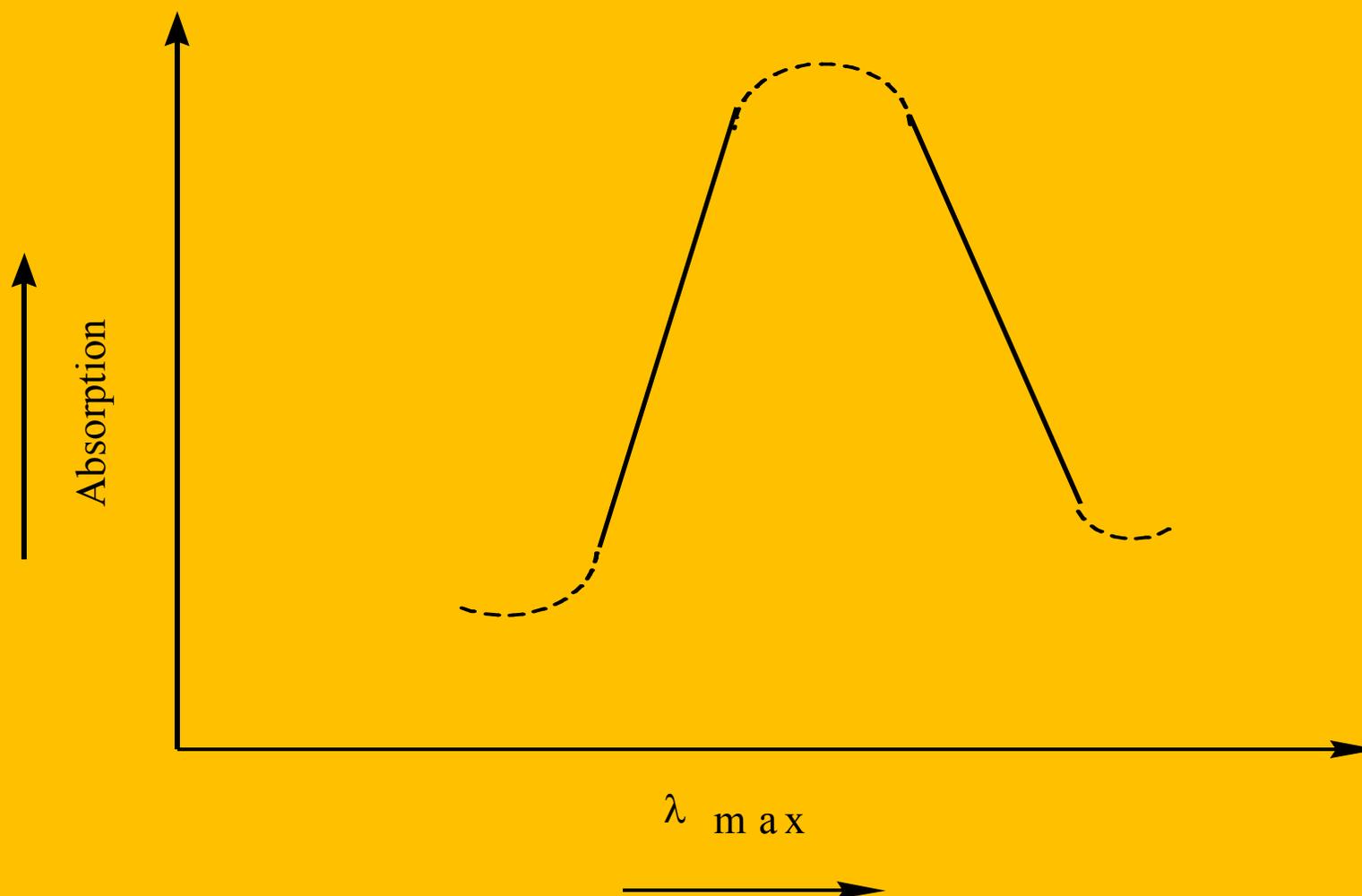
Some electronic transitions, which are otherwise theoretically possible, are generally not observed in the UV/VIS spectroscopy. Therefore there are some restrictions which govern the observable transitions.

1. Transitions, which involve change in the spin quantum number of an electron during the transitions do not occur, i.e. singlet-triplet transitions are not allowed.

2. Transitions between orbitals of different symmetry do not occur. For example, transition n to π^* is forbidden because the symmetry of n and π^* do not match.

❖ UV OR ELECTRONIC SPECTRUM:

In the UV visible spectroscopy the spectrum are to be plotted between absorption and wavelength a general UV visible spectrum can be represented-



Where λ_{max} is the wavelength corresponding to the maximum absorption.

In case of UV visible spectroscopy the peaks are founded to be broader because this spectroscopy involved the electronic transition in which vibrational as well as rotational transition also occurs.

❖ **CHROMOPHORE AND AUXOCHROMES:**

➤ **CHROMOPHORE:** *Any isolated covalently bonded groups shows a characteristic absorption in the UV or visible region. Ethylene, Acetylene, carbonyl, carboxylic acid, ester groups are important chromophore.*

➤ **Types of chromophore:**

1. π electron contain groups eg. Ethene and ethyne or acetelene

1. π electron containing groups as well as heteroatom eg. Carbonyls, Nitriles and nitro compounds.

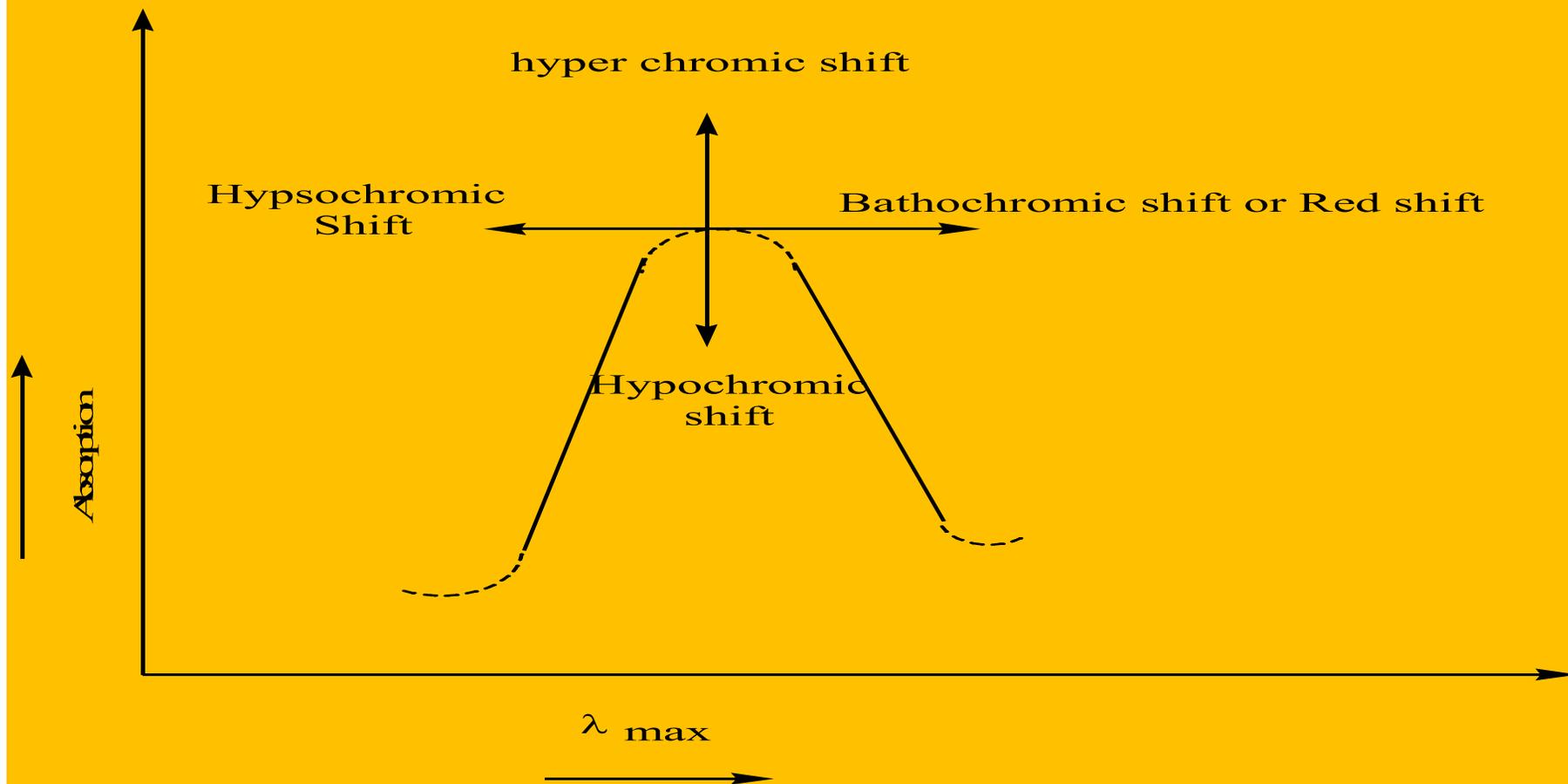
2. **AUXOCHROMOES:**

The Auxochromes can be defined as any groups which does not itself act as achromosomes but whose presence bring bout a shift of the absorption band towards the longer wavelength of these spectrum.

Auxochrome + Chromosome = New Chromosomes

Examples: All the +M effective groups like OH, NH₂, NH₂R, R₂NH, R₃N etc.

❖ *ABSORPTION AND INTENSITY SHIFT*



1. Red shift or bathochromic shift-

The presence of auxochrome may result in a shift of absorption maxima towards longer wavelength which is called bathochromic or red shift. Bathochromic shift may also observe due to change in solvent polarity that will result in solvatochromism.

2. Blue shift or hypsochromic shift-

The presence of auxochrome may result in a shift of absorption maxima towards shorter wavelength which is called hypsochromic shift or blue shift.

3. Hyperchromic effect:-

An increase in absorption intensity due to presence of substituent with chromophore is called hyperchromic effect.

4. Hypochromic effect:- A decrease in absorption intensity due to presence of substituent with chromophore is called hypochromic effect.

❖ **ABSORPTION BAND:**

Depending on the nature of transition of band, Absorption band can be of the four types.

1. R- band (Radical band)
2. K –band (Kanjugation)
3. B-band (Benzonoid band)
4. E –band (Ethylinic band)

1. R- band (Radical band):

Such type of the band is originated due to the n to π^* or n to σ^* transition. Eg. Alcohol, Alkyl Halide, carbonyl compounds etc.

2. K –band (Kanjugation):

K band is originated from the compounds which containing conjugated system. This type of band originated by π to π^* transition. Eg. Unsaturated hydrocarbons like diene, polyene, enones etc.

3. B- band:

Such type of the band appeared in the benzenoid compounds. These band originated from π to π^* transition in aromatic compound.

4. E-band:

Such type of the band originated due to three ethylinic band in the aromatic compounds. This band occur in the π to π^* transition.

❖ RELATION BETWEEN ABSORPTION AND EMISSION SPECTRA

(Lambarts- Beeyer's law)

It gives a linear relationship between absorbance and concentration of an absorbing species. *This law states that the absorption is directly proportional to the concentration of absorbing substance and the length of the path of radiation through the sample.*

It is independent of the intensity of the incident light and each successive unit layer absorbs an equal fraction of light incident on it.

$$A = \epsilon cb$$

$$\text{Log}_{10} I_0/I = \epsilon cb$$

Where A is the sample's Absorbance value at specific wavelength or frequency

ϵ is the molar absorptivity or the molar extinction coefficient of the substance

b is the path length of the sample in cm

c is the concentration of the solute in mol L⁻¹.

The value of ϵ absorptivity coefficient is constant for a particular material at a particular wavelength.

➤ **Limitations of the Beer-Lambert Law:**

Under certain conditions Beer-Lambert law fails to maintain a linear relationship between absorbance and concentration of the solution.

1. Deviations in absorptivity coefficients at high concentrations (>0.01M) due to electrostatic interactions between molecules in close proximity.

2. Scattering of light due to particles present in the sample.
3. Chemical deviations due to the specific chemical species of the sample under investigation.
4. Non-monochromatic radiation
5. Fluorescence or phosphorescence of the sample.

THANK YOU